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A METHOD FOR THE SEPARATION AND GRAVIMETRIC DETERMINATION OF OSMIUM

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ABSTRACT

A procedure for the separation and gravimetric determination of osmium is described. This procedure involves the separation of osmium from other metals by distillation as the volatile tetroxide and its recovery from solution by hydrolytic precipitation. A very suitable reagent for the quantitative absorption of the distilled tetroxide was found to be 6 normal hydrochloric acid saturated with sulphur dioxide. The recovery of osmium was accomplished by precipitating the hydrated dioxide from a boiling solution at acidities ranging from pH 1.5 to 6.3, after sulphite compounds had been decomposed by repeated evaporation with hydrochloric acid. The hydrated dioxide was impregnated with ammonium chloride to prevent mechanical loss when ignited to metal under hydrogen.

The thiourea test devised by Chugaev for the detection of small quantities of osmium was modified so that it could be applied to solutions containing nitric acid. The test was found to be sensitive to 1 part in 5,000,000 parts of solution, which is 50 times as sensitive as stated by Chugaev.

CONTENTS

		Page
I.	Introduction	422
	1. Method of Ruff and Bornemann	425
	2. Method of Ogburn and Miller	426
II.	Object of the investigation	427
III.	Preparation of osmium compounds for use in the experiments	428
IV.	Precipitation of hydrated osmium dioxide by hydrolysis	430
V.	Effect of exposure of osmium sponge to the air	430
VI.	Qualitative experiments to determine the completeness of precipitation of hydrated osmium dioxide	431
VII.	Detection of minute quantities of osmium by reaction with thiourea	431
VIII.	Choice of crucibles for filtration	433
IX.	Range of pH values over which hydrated osmium dioxide is completely precipitated by hydrolysis	433
X.	Separation of osmium by distillation and recovery by hydrolysis	434
XI.	Experiments to locate the source of error in the determination of osmium by distillation from solution with nitric acid	437
XII.	Complete recovery of osmium from solutions of hydrochloric acid which have contained sulphur dioxide	439
XIII.	Precipitation of osmium in the presence of sodium salts	440
XIV.	Separation of osmium from the other platinum metals by distillation from nitric-acid solution	441
XV.	Incidental experiments	442
	1. Distillation from a mixture of sulphuric and nitric acids	442
	2. Distillation from sulphuric acid	443
	3. Distillation from nitric acid	443
	4. Distillation from alkaline solution acidified with nitric acid	443
XVI.	Summary of results obtained	445
XVII.	Method of analysis recommended	446
	1. Distilling apparatus	446
	2. Procedure	447
XVIII.	Acknowledgments	448

I. INTRODUCTION

The most outstanding property of osmium is the formation of a volatile oxide of the composition OsO_4. This oxide is produced when solutions of osmium are treated with oxidizing reagents or when solutions containing compounds of osmium decompose under certain conditions. It is also produced when osmium is heated in an atmosphere either of air or of oxygen and even when osmium sponge is allowed to remain in contact with air at room temperature. It might well be said that the chemistry of osmium revolves about this oxide, since any work with this element is almost certain to involve at some stage the formation of the tetroxide.

The ready formation of the tetroxide of osmium is made use of in separating osmium from the other platinum metals, not only for purposes of refining, but also for purposes of analysis. The tetroxide melts at about 40° C.,[1] [2] boils at 129° C.[2] and can be distilled from aqueous solution. According to Deville and Debray,[3] who determined the vapor density of osmium tetroxide, the compound is stable at temperatures up to 285° C. More recently, von Wartenberg[4] found that the tetroxide is not decomposed at temperatures up to 1,500° C.

While the vapor of osmium tetroxide shows an astounding degree of stability when pure or in the presence of oxygen, it is extremely unstable if reducing substances, such as alcohol, formaldehyde, hydrazine, etc., are present. Reduction, however, usually goes only to the dioxide[5] and not to the metal.

Thus the tendency of osmium to form tetroxide, which may escape, introduces difficulties into the quantitative handling of the element, while the readiness with which the tetroxide suffers reduction in the presence of organic matter further complicates the transfer of osmium tetroxide by distillation. For instance, the apparatus used must be constructed wholly of glass and no organic lubricant can be used on ground joints.

The method employed for the determination of the osmium content of a material will depend to a great extent upon the nature of the material. In many of the pure compounds of osmium, such as ammonium chloroosmate $(NH_4)_2OsCl_6$, ammonium bromoosmate $(NH_4)_2\ OsBr_6$, etc., the determination can be made simply by heating the substance in an atmosphere of hydrogen. The resulting product, which will consist only of metallic osmium, is then weighed. If the compound be potassium chloroosmate (K_2OsCl_6), potassium bromoosmate (K_2OsBr_6), etc., it becomes necessary, in addition, to remove the soluble alkali salt from the resulting osmium sponge by leaching with water.

Such methods as those just mentioned are of little use, however, when the osmium is present in solution with other metallic elements or combined in such materials as crude platinum, osmiridium, etc. It then becomes necessary to make first a separation of the osmium from the elements which accompany it. This separation is usually

[1] F. Krauss and D. Wilken, Z. anorg. allgem. Chem., **145**, p. 151; 1925.
[2] H. von Wartenberg, Ann., **440**, p. 97; 1924.
[3] H. Ste-C. Deville and H. Debray, Ann. des Mines, (5) **16**, p. 22; 1859. Encyclopédie Chimique, 30 (1), p. 73.
[4] See footnote 2.
[5] C. Paal and C. Amberger, Ber., **40**, p. 1378; 1907.

accomplished by the formation of osmium tetroxide, which is distilled from solution and recovered by absorption in some reagent.

A number of gravimetric methods have been investigated for the removal of osmium from the absorbent solutions and for the conversion of the precipitate to a weighable form. A survey of these methods shows that, in nearly every case, the precipitate which is removed from the absorbent solution consists of hydrated osmium dioxide, and that the difference in the methods is merely the manner in which the precipitate is obtained and subsequently treated. In addition to gravimetric methods, at least one volumetric procedure has been proposed, in which the osmium as tetroxide is reduced to quadrivalent osmium, liberating free iodine, which is titrated with a solution of sodium thiosulphate.

Paal and Amberger [6] made a notable contribution by studying not only the gravimetric methods known at the time, but also by investigating various other possible analytical procedures. Although the results obtained by these authors are described in detail in the reference mentioned, a brief description of their methods and results may help to make clear the difficulties encountered in the determination of osmium.

1. A procedure which involved the separation of osmium from alkaline osmate solutions in the form of Frémy's salt, osmyl tetrammine chloride, $OsO_2\ (NH_3)_4Cl_2$, by precipitation with ammonium chloride in a solution of hydrochloric acid, and subsequent reduction of the compound obtained to metal [7] in hydrogen, gave recoveries of osmium which varied considerably and were roughly 10 per cent short of the quantities of osmium taken. This procedure was rejected by Paal and Amberger as unusable.

2. The method of Leidié and Quennessen [8] which consisted of the precipitation of metallic osmium from alkaline solutions of sodium osmate by aluminum, was found to give incomplete precipitation of osmium. Furthermore the precipitate was contaminated by compounds of aluminum. It was found that the precipitate produced was not metallic osmium, as thought by Leidié and Quennessen, but osmium dioxide. The results obtained by the method were too low to establish it as a usable procedure.

3. A statement by Frémy [9] that osmium disulphide was precipitated from solutions of potassium osmate (K_2OsO_4), by hydrogen sulphide, led Paal and Amberger to consider this reaction as a possible means of recovering osmium from solutions of osmium tetroxide in sodium or potassium hydroxide to which alcohol has been added. The alkaline solution was treated with hydrogen sulphide, then made acid with dilute sulphuric acid and again saturated with hydrogen sulphide. The precipitate obtained was found not to be the disulphide, but a hydrated oxysulphide of similar composition to that obtained by von Meyer [10] by the action of hydrogen sulphide on osmium tetroxide. Von Meyer stated that he was able to obtain osmium free from sulphur by igniting this precipitate in hydrogen, a goal which Paal and Amberger were unable to attain. At times osmium was found to be present in the filtrates and in the wash

[6] See footnote 5, p. 422.
[7] A. Classen, Ausgewählte Methoden der analyt. Chem., **1**, p. 277; 1901.
[8] E. Leidié and L. Quennessen, Bull. Soc. Chim. (3), **29**, p. 805; 1903.
[9] E. Frémy, Ann. chim. phys. (3), **12**, p. 521; 1844.
[10] E. von Meyer, J. prakt. Chem. (2), **16**, p. 77; 1877.

waters. The recoveries varied widely, being sometimes greater than the quantities of osmium taken, so that determinations based upon this procedure were unreliable.

4. The use of hydrazine hydrate in the production of colloidal osmium preparations from alkaline osmate solutions was extended by Paal and Amberger in order to determine whether this reagent could be used to precipitate osmium for analytical purposes. The filtrates were found to contain considerable quantities of osmium while the precipitates which were obtained were very difficult to filter. When applied to solutions of osmium tetroxide in alcohol, diluted somewhat with water, hydrazine hydrate caused reduction to commence immediately, but the precipitation did not always behave in the same manner under apparently similar conditions. Warming the solution appeared to hasten the precipitation while the presence of ammonium chloride hindered it. The precipitate obtained was not osmium, but again the hydrated dioxide.

5. Another possibility which Paal and Amberger considered was the absorption of osmium tetroxide in a solution of ammonium hydroxide and ammonium chloride, evaporation of the resulting solution to dryness on the steam bath, and the reduction of the residue to metal in hydrogen. The average value found in three experiments was about 1.5 per cent less than the quantity of osmium taken. The authors considered that this method gave too low results.

6. Two other possibilities, which consisted in the treatment of solutions of osmium tetroxide in alcohol by formaldehyde and by the acetaldehyde produced by the action of sunlight, gave precipitates of hydrated dioxide and results which were low by about 0.4 to 0.6 per cent. Difficulty was encountered in the coagulation, settling, and filtration of the precipitates obtained, the filtration taking from one to two days.

7. Included in this series of studies was a volumetric method of Klobbie[11] based on the reaction of osmium tetroxide with potassium iodide in acid solution. The iodine liberated by the reduction of osmium tetroxide to quadrivalent osmium was titrated with $N/100$ sodium thiosulphate. Experiment showed that for more concentrated solutions the results varied widely and only from 83 to 95 per cent of the osmium tetroxide taken was found. Paal and Amberger concluded that this method was apparently applicable only to very dilute solutions.

8. As a result of their investigations Paal and Amberger developed a method which they considered gave them the best results. According to the observations of Frémy[12] and of Claus,[13] pure osmate solutions decompose on acidification with the formation of osmium dioxide and of osmium tetroxide. Moraht and Wischin[14] found that if alcohol is present the osmium is precipitated from solution as a finely divided hydrated oxide which could be obtained free from alkali only by washing with water for a number of days. Paal and Amberger's procedure consisted in the conversion of osmium tetroxide, in a solution of potassium hydroxide and alcohol, into potassium

[11] E. A. Klobbie, Chem. Zentralbl., **2**, p. 65; 1898.
[12] Frémy, J. prakt. Chem. (1), **33**, p. 467; 1844; (1), **34**, p. 308; 1845.
[13] C. Claus, J. prakt. Chem. (1), **34**, p. 420; 1845.
[14] H. Moraht and C. Wischin, Z. anorg. Chem., **3**, p. 153; 1893.

osmate, K_2OsO_4, by heating the solution at 40° to 50° C. An excess of alcohol was kept present in order to reduce any osmium tetroxide which was formed. The solution was acidified with dilute sulphuric acid, in slight excess, and allowed to remain for 10 to 12 hours. The black precipitate which settled out was separated from the colorless mother liquor by filtering through a tube having an asbestos pad. The precipitate was washed with a solution of water and alcohol until sulphuric acid was eliminated, drained as dry as possible by suction, and placed in a desiccator over caustic soda. In order to prevent the formation of tetroxide, alcohol vapor was kept in the desiccator. The precipitate was reduced to metal by carefully heating it in hydrogen, the apparatus having been first freed from air by carbon dioxide. The average result of three experiments showed that recovery of the osmium was about 0.25 per cent less than the quantity taken.

1. METHOD OF RUFF AND BORNEMANN

Ruff and Bornemann[15] modified the method of Paal and Amberger as a result of the observation that the formation of a colloidal solution was wholly avoided if care were taken to establish complete neutrality of the alkaline osmate solution while it was heated on the steam bath. In the hands of Ruff and Bornemann, the method of Paal and Amberger was adapted to the analysis of chloride and of fluoride compounds of osmium as follows:

The chloride or fluoride was dissolved in a solution of caustic alkali containing alcohol and heated on the water bath either in a platinum dish or in a beaker of resistance glass. The excess of alkali was neutralized, while the solution was hot, with either 2 normal sulphuric acid or with hydrochloric acid, using phenolphthalein as indicator, and the solution allowed to stand on the water bath. Additional acid was added from time to time to discharge the recurring pink color of the indicator. When the hydrated osmium dioxide settled out, leaving the mother liquor colorless, the reaction was regarded as complete. Since the hydrated dioxide so obtained could not be heated at temperatures from 100° to 150° C. without undergoing explosive decomposition, Ruff and Bornemann attempted to diminish this tendency to deflagrate by allowing the precipitate and solution to remain on the water bath an additional six hours. They found also that the precipitate was difficult to filter and to wash. The precipitate was dried by gradually heating it to 150° C. in a current of carbon dioxide laden with alcohol vapor, then in a current of pure carbon dioxide to 250° C., and weighed as anhydrous osmium dioxide, OsO_2. A supplementary determination was made by then igniting the anhydrous dioxide to metal in hydrogen.

This procedure of Paal and Amberger, modified in some details by Ruff and Bornemann, is undoubtedly the best of the published methods for the determination of osmium. There are a number of features about it, however, which make it troublesome to use. For instance, if glass beakers are employed the precipitate is contaminated by silica which has been dissolved by the hot alkaline solution. A correction for the silica can be made only by igniting the metallic residue in air or in oxygen, the osmium being then either lost or

[15] O. Ruff and F. Bornemann, Z. anorg. Chem., 65, p. 429; 1910.

requiring the additional trouble of subsequent recovery. The time required to prepare the precipitate for filtration is far too great, and hydrated oxides produced from alkaline solutions appear to have considerable tendency to become colloidal during washing. Howe and Mercer[16] found this to be the case with hydrated ruthenium oxide hydrolyzed from alkaline solutions. Furthermore, there appears to be a tendency for such precipitates to retain alkali, probably by adsorption, so that even long continued washing may not always be effective. Perhaps the chief difficulty in the method and the one which requires care, patience, and cumbersome apparatus to overcome is the conversion of the hydrated dioxide to metal. Both Paal and Amberger, and Ruff and Bornemann found that the hydrated dioxide of osmium deflagrated on heating, and elaborate precautions were taken to avoid the consequent mechanical loss of osmium. These investigators attributed the phenomenon to the removal of water from the hydrated compound. Deville and Stas[17] observed the same behavior in the ignition of hydrated iridium dioxide, while in earlier work[18] in this laboratory it was found that the most difficult step in the development of a gravimetric method for the determination of ruthenium was eliminating the tendency of the hydrated oxide to deflagrate when it was ignited to the anhydrous oxide.

2. METHOD OF OGBURN AND MILLER

In a recent article by Ogburn and Miller[19] a method was proposed for the determination of osmium, using strychnine sulphate as a precipitating reagent. The authors state that when a saturated solution of strychnine sulphate is added to a slightly acidified solution of sodium chloroosmate (Na_2OsCl_6) the osmium is completely precipitated as a heavy canary yellow compound and that no osmium can be detected in the supernatant liquor by hydrogen sulphide or by thiourea. They state further that the compound contains neither chlorine nor the sulphate radical, and that it is probably composed of one atom of osmium combined with three strychnine radicals, $(C_{21}H_{22}O_2N_2)_3Os$. However, in determining osmium by drying and weighing the precipitate, the empirically determined factor 0.1758 was used. No explanation is given for the discrepancy between this factor and that calculated from the postulated formula, which is 0.1599.

The writer made a number of trials of the method of Ogburn and Miller, in which their directions were carefully followed, except that larger quantities of osmium were taken, to minimize errors of weighing, etc., and with the further exception that weighed portions of ammonium chloroosmate and of ammonium bromoosmate, of known osmium content, were used instead of the solution of sodium chloroosmate used by Ogburn and Miller. It was found that the filtrates invariably contained osmium, apparently because some solution of the precipitate occurred during washing. Furthermore, the precipitate formed by adding strychnine sulphate to the solution of chloroosmate was not identical with that formed from the bromoos-

[16] Jas. L. Howe and F. N. Mercer, J. Am. Chem. Soc., **47**, p. 2926; 1925.
[17] H. Ste-C. Deville and J. S. Stas, Procès-verbaux, Comité International des poids et mesures, p. 195; 1877.
[18] R. Gilchrist, B. S. Jour. Research, **3**, p. 993; 1929.
[19] S. C. Ogburn, jr. and L. F. Miller, J. Am. Chem. Soc., **52**, p. 42; 1930.

mate, either in color or in osmium content, the latter being brown rather than yellow, and containing about 15.8 per cent of osmium as compared with about 19.1 per cent for the compound prepared from the chloroosmate. These values for the osmium content are not to be regarded as accurate. They are probably slightly high because they were determined from the weight of osmium actually taken and the weight of the precipitate formed, without correcting for the small amount of osmium left in the filtrates. However, they are amply accurate to indicate a real difference in composition between the two precipitates. Also, in the case of the compound prepared from the chloroosmate, the value differs too much from the value given by Ogburn and Miller to warrant the opinion that the composition of the compound is definite enough, except possibly under very closely regulated conditions, to permit determining osmium by the use of an arbitrary factor.

The two compounds formed were qualitatively examined for the presence of chlorine and bromine with the expectation of accounting for the differences in color and osmium content. Quite contrary to the findings of the authors that their compound contained no chlorine, the two compounds were found to yield considerable amounts of halogen. In view of the inconstancy of composition of the precipitates, and because of the failure to get quantitative precipitation, it appeared that the method proposed by Ogburn and Miller could not be regarded as reliable, at least in its present form.[20]

II. OBJECT OF THE INVESTIGATION

The object of the experiments reported in this paper was the development of an accurate method for the determination of osmium which would be as simple and as rapid as possible. As seen from the previous discussion no satisfactory method had so far been developed.

The determination of osmium in a material, such as crude platinum, osmiridium, etc., ordinarily involves solution of the original material; separation of osmium from accompanying elements, usually by distillation as tetroxide; absorption of the tetroxide in some reagent solution with subsequent recovery of the osmium and its conversion to a weighable form. It has been generally assumed that the separation of osmium from other elements by distillation of osmium tetroxide is complete, but the literature does not disclose any thoroughgoing quantitative study of this subject. The experiments reported here were directed principally toward a method determination, but incidental work was done to determine the completeness of the separation of osmium by the usual method of distillation. The experiments were not extended to methods of effecting solution of raw platiniferous materials.

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[20] In view of the behavior of strychnine in forming salts by direct addition of acids, it is interesting to speculate whether, in its reaction with osmium (and the known reactions with the other platinum metals), strychnine is not acting simply like the ammonium radicle and forming strychnine chloroosmate $(C_{21}H_{22}O_2N_2)_2{-}H_2OsCl_6$, and strychnine bromoosmate, $(C_{21}H_{22}O_2N_2)_2{-}H_2OsBr_6$. The properties of the compounds tend to suggest this structure and the calculated osmium content of strychnine chloroosmate, 17.76 per cent, corresponds much more closely with Ogburn and Miller's average value 17.58 per cent, than does the osmium content of the compound postulated by them. If such compounds were being precipitated from solutions of ammonium or alkali choloroosmate or bromoosmate it is not impossible that mixed crystals of the strychnine and these ammonium or alkali compounds would be formed. The formation of mixed crystals with the less soluble ammonium or potassium salts would be more likely than with the very soluble sodium salts. The presence of such mixed crystals in the preparation referred to in this paper would account for its having a greater osmium content than that calculated for strychnine chloroosmate and that of the preparation of Ogburn and Miller.

III. PREPARATION OF OSMIUM COMPOUNDS FOR USE IN THE EXPERIMENTS

The osmium used was purified by the method described in an earlier paper [21] from this laboratory. The osmium was distilled from a solution containing nitric acid, the tetroxide absorbed in a solution of sodium hydroxide and the distillation and absorption repeated. The alkaline osmate solution from the second distillation was neutralized with hydrochloric acid and the osmium recovered as hydrated osmium dioxide. This product was washed with water by decantation and sucked as dry as possible on a filter. The dioxide was reduced to metallic osmium by strong ignition in hydrogen.[22] The reduced metal, which was free from the other platinum metals, was carefully ignited to osmium tetroxide in a current of oxygen. The tetroxide was recovered by condensation and converted, in one instance, into chloroosmic acid, (H_2OsCl_6) and in the other, into bromoosmic acid (H_2OsBr_6).

The conversion of the tetroxide into chloroosmic acid was accomplished by heating the tetroxide with four times the theoretical quantity of 6 normal hydrochloric acid to which about 5 ml of alcohol had been added. The reaction flask was connected to a reflux condenser by a ground-glass joint. The end of the reflux condenser was fitted to a trap containing a solution of sodium hydroxide and alcohol to catch the small amount of osmium tetroxide which passed the condenser. The reaction mixture was heated gently at first and the temperature very gradually increased during three hours to incipient boiling. The osmium tetroxide was gradually reduced to quadrivalent osmium chloride, completion of the reaction being shown by the absence of droplets of osmium tetroxide condensing on the walls of the flask, the change of color of the solution to a clear transparent red, and the absence of the characteristic odor of osmium tetroxide. The solution of chloroosmic acid was evaporated to a sirup on the steam bath and then twice evaporated with hydrochloric acid (specific gravity 1.18). The sirupy residue was dissolved in dilute hydrochloric acid (1 volume of acid of specific gravity 1.18 diluted with 9 volumes of water) and filtered through paper. Ammonium chloroosmate was precipitated by slowly adding a saturated solution of ammonium chloride to this solution. The brick-red precipitate was caught on a hardened filter and washed first with a solution of ammonium chloride and finally with alcohol. The precipitate was sucked as dry as possible, dried over phosphorus pentoxide in a desiccator for some time, then intimately mixed by grinding in an agate mortar, and stored over phosphorus pentoxide in a desiccator until used.

The conversion of osmium tetroxide into bromoosmic acid and finally into ammonium bromoosmate was accomplished in the same manner as described for the chloro compound, the difference being that hydrobromic acid was used in place of hydrochloric acid. The reduction with hydrobromic acid takes place more readily than with

[21] E. Wichers, R. Gilchrist, and W. H. Swanger, Trans. Am. Inst. Mining Met. Eng., 76, p. 602; 1928.

[22] Later experience has shown that this procedure is probably not desirable because of danger of deflagration. In the work here reported the presence of sodium chloride, resulting from incomplete removal by washing, no doubt prevented deflagration. It would be better to impregnate the precipitate with ammonium chloride prior to drying and ignition, or alternatively to dissolve the precipitate in hydrochloric acid and precipitate the osmium as ammonium chloroosmate.

hydrochloric acid. Ammonium bromoosmate is deep brown, almost black in color and forms a deep brown solution in water.

It is perhaps needless to mention that no attempt was made to prepare compounds of definite composition, but merely to prepare compounds which could be ignited directly to pure osmium. The osmium content of the samples used was never calculated from the theoretical formula, but was always determined whenever a series of samples was weighed. For this purpose a few samples were taken at random and ignited to metal in hydrogen. The sample was placed in a porcelain crucible which was then covered with a perforated quartz lid. A gentle flame was directed against the top of the lid and a stream of hydrogen, burning from the tip of a quartz delivery tube, was introduced through the hole in the lid. After about 10 minutes a second flame was placed beneath the crucible, and the osmium salt was slowly and very cautiously decomposed. When the resulting metallic sponge began to contract, the temperature of the second flame was gradually increased to that of the full heat of the burner. After 20 minutes both flames were removed and when the crucible had cooled somewhat, the hydrogen flame was extinguished by momentarily breaking the current of hydrogen. The hydrogen was finally displaced by carbon dioxide and the crucible allowed to cool to room temperature. After weighing, the metallic sponge was again heated in hydrogen for 20 minutes and cooled as just described. In so doing no significant changes of weight were observed. The average value found was used to calculate the osmium present in the remaining portions used for experiment.

The values found for the osmium content of the preparations of ammonium chloroosmate and of ammonium bromoosmate used in the investigation are given in Table 1.

TABLE 1.—*Determination of the osmium content of the preparations of ammonium bromoosmate and of ammonium chloroosmate used*

No.	$(NH_4)_2OsBr_6$	$(NH_4)_2OsCl_6$	Osmium	Osmium	Tables
	g	*g*	*g*	*Per cent*	
1	0.5134	----------	0.1440	28.05	2, 3.
2	.4362	----------	.1224	28.06	
3	.3892	----------	.1092	28.06	
4	.5942	----------	.1668	28.07	
5	.4673	----------	.1311	28.05	
6	.3567	----------	.1001	28.06	
				28.06	
7	.3946	----------	.1063	26.94	4, 5.
8	.4915	----------	.1322	26.90	
9	.4161	----------	.1119	26.89	
				26.91	
10	.4818	----------	.1297	26.92	3, 5, 7.
11	.5729	----------	.1544	26.95	
12	.6789	----------	.1830	26.95	
				26.94	
13	----------	0.4482	.1760	39.27	2.
14	----------	.7449	.2927	39.29	
				39.28	
15	----------	.2559	.1111	43.42	3.
16	----------	.2561	.1112	43.42	
17	----------	.2346	.1018	43.39	
				43.41	

IV. PRECIPITATION OF HYDRATED OSMIUM DIOXIDE BY HYDROLYSIS

Preliminary experiments were made in which hydrated osmium dioxide was precipitated, according to the directions of Ruff and Bornemann, from solutions of sodium hydroxide containing some alcohol to which were added known quantities of chloroosmic acid (H_2OsCl_6). The precipitate, in each instance, was caught on an asbestos filter in a porcelain crucible and reduced in hydrogen, the crucible being covered with a perforated quartz lid and shielded from the burner flame by a second crucible. Deflagration of the precipitate nearly always occurred within one or two minutes after the introduction of the burning hydrogen and before heat was applied to the under side of the protecting crucible. In some instances no deflagration occurred. Here it was found that the weight obtained after strong ignition in hydrogen was excessively high. No consistent results could be obtained, and on ignition the metallic residues were found to be contaminated with silica, those which did not deflagrate showing the greatest contamination.

After these preliminary experiments the work on osmium was interrupted by similar work on a method for the determination of ruthenium.[23] In the experiments with ruthenium it was found that quantitative precipitation by hydrolysis could be easily and quickly accomplished from the acid side and that the precipitate was not contaminated by silica or by alkali. Furthermore, it was found that the presence of ammonium salts eliminated the danger of deflagration when the dried precipitate was ignited.

By following the procedure developed for ruthenium, the difficulties previously encountered with osmium vanished and excellent recoveries were obtained. In one experiment, where a Munroe crucible was used instead of a Gooch crucible, 0.01305 g of osmium as H_2OsCl_6 was taken, and 0.0130 g was recovered. In a second similarly conducted experiment in which ten times the quantity of osmium was taken, 0.1305 g of osmium was recovered. The technic of handling the precipitated osmium dioxide differed somewhat from that with the ruthenium oxide and will be discussed more fully in a later section of this paper.

V. EFFECT OF EXPOSURE OF OSMIUM SPONGE TO THE AIR

Since the osmium obtained, both by direct ignition of the ammonium compounds and by ignition of the recovered dioxide, is weighed as metallic sponge it is important to know just what effect exposure to the air has upon the sponge. It had been observed in this laboratory that osmium sponge, produced by igniting ammonium chloroosmate or ammonium bromoosmate in hydrogen in a combustion tube, glowed and emitted pungent vapors of osmium tetroxide when the tube was opened, even at room temperature. If, however, the hydrogen had been displaced by dry purified nitrogen while the osmium sponge was hot and the metal had been allowed to cool in nitrogen no odor of osmium tetroxide was observed and the sponge suffered no change in weight on standing in the air for some time.

[23] See footnote 18, p. 426.

In the procedure used in the experiments reported here the osmium was not ignited in a combustion tube but in a crucible, either of porcelain or of platinum, and carbon dioxide was used to displace the atmosphere of hydrogen. In order to ascertain the reproducibility of weight when such a procedure was followed, portions of osmium sponge, resulting from the reduction of ammonium bromoosmate, were repeatedly ignited in hydrogen, cooled in carbon dioxide, and weighed. It was found that no significant changes of weight occurred during such operations and in addition that no changes of weight were observed, even when the sponge had remained in a desiccator over a period of two weeks.

VI. QUALITATIVE EXPERIMENTS TO DETERMINE THE COMPLETENESS OF PRECIPITATION OF HYDRATED OSMIUM DIOXIDE

It was observed, as it was with ruthenium, that as the boiling acidified solution of osmium was gradually neutralized by the addition of sodium bicarbonate, a precipitate suddenly coagulated and settled. With ruthenium, this coagulation and separation represented complete precipitation. Qualitative experiments were made to determine whether the same was true with osmium. Portions of ammonium bromoosmate were dissolved in 150 ml portions of water. A 10 per cent solution of sodium bicarbonate was slowly added to the boiling solutions until coagulation occurred. One solution was then boiled for 15 minutes and the other for 6 minutes and filtered through S. and S. No. 589 blue ribbon paper. The filtrates were colorless and clear, and had acidities which were between the pH values 1.5 and 4.0. A sample of ammonium chloroosmate was also treated as described and the solution boiled for six minutes. In this instance the acidity of the water clear filtrate was estimated, by means of indicator solutions, to be approximately 2.8 to 3.0. The filtrates were tested for the presence of osmium by means of thiourea as described in a subsequent paragraph. No osmium was detected in any of the filtrates.

An experiment was also made to determine whether a loss of osmium as osmium tetroxide occurred during hydrolysis. In this instance the neutralization with sodium bicarbonate was done in a distilling apparatus composed wholly of glass and the solution was finally boiled for one-half hour while a slow current of air was passed. The vapors which distilled were absorbed in a solution of 6 normal hydrochloric acid saturated with sulphur dioxide to which thiourea was added. This solution developed no pink color when heated. As 0.1 mg of osmium would have been readily detected, it was evident that no loss occurred.

VII. DETECTION OF MINUTE QUANTITIES OF OSMIUM BY REACTION WITH THIOUREA

It very soon became necessary to be able to detect small quantities of osmium, particularly in the filtrates from hydrolysis and in the residual nitric acid solutions after osmium had been distilled as tetroxide.

The most delicate known reaction for the detection of osmium is that discovered by Chugaev [24] during his researches on osmium compounds. Chugaev found that when a solution containing osmium tetroxide or potassium chloroosmate, acidified with a few drops of hydrochloric acid, is heated with thiourea for a few minutes a deep red or rose color develops. He also found the limit of sensitivity to be 1 part in 100,000 parts of solution.

The test as described by Chugaev, however, can not be applied directly to a solution containing a considerable quantity of nitric acid, since this acid decomposes the reagent. It was found, however, that if the nitric acid is destroyed by reaction with sulphur dioxide the color with thiourea will develop and be stable. Experiments with known quantities of osmium showed that under these conditions the limit of sensitivity is 1 part in 5,000,000 parts of solution, and

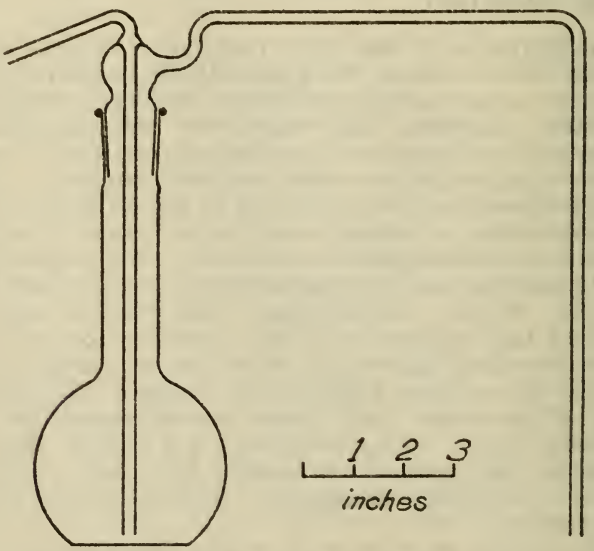

FIGURE 1.—*Distilling flask for osmium tetroxide*

that for concentrations greater than 1 part in 2,500,000 the pink color develops in less than 15 minutes. The sulphur dioxide may be conveniently added in the form of solution in water, and it is well to have it present in excess. Only a few small crystals of thiourea are required, and it is necessary only to heat the solution on the steam bath.

The presence of indicators, such as brom cresol purple, brom phenol blue, etc., masks the color produced by thiourea so that when filtrates from hydrolysis were being investigated the osmium had to be removed by distillation with nitric acid from an apparatus composed wholly of glass (shown in fig. 1) and absorbed in a solution of 6 normal hydrochloric acid saturated with sulphur dioxide and containing a little thiourea. The distillation of osmium tetroxide was aided by passing a current of air through the apparatus.

[24] L. Chugaev, Compt. rend., 167, p. 235; 1918.

VIII. CHOICE OF CRUCIBLES FOR FILTRATION

In gravimetric procedures for determining osmium it is obviously impossible to use filter paper, because oxidation of osmium to the volatile tetroxide will occur when the paper is destroyed by ignition in air.

In the methods discussed in the introductory part of this paper, filtering tubes containing pads of asbestos were used to recover the precipitate of osmium dioxide. It was found that a Gooch crucible with an asbestos pad, prepared in the usual way and ignited to constant weight, can be used. Care must be taken, however, in the preparation of the asbestos used as a filter. In a series of five experiments, in which the hydrated osmium dioxide was hydrolyzed from solutions of ammonium chloroosmate at pH values ranging from 4.0 to 6.3, it was observed that a small quantity of precipitate passed through the asbestos filters. The errors found were from -0.0001 to -0.0010 g of osmium on 0.20 to 0.24 g of osmium taken, and these amounts were readily detected in the filtrates. In a second, more carefully conducted, series of five experiments, in which the hydrated dioxide was precipitated from solutions of ammonium bromoosmate at pH values ranging from 4.0 to 6.0, the errors observed in four of the experiments varied from $+0.0001$ to -0.0001 g of osmium, while in the fifth the error was -0.0003 g. When these filtrates were filtered through S. & S. No. 589 blue ribbon papers, no blackening of the papers was observed except in the case of the one showing the error -0.0003 g.

The chief disadvantage in the use of a Gooch crucible with an asbestos pad is the difficulty encountered during the ignition of the dioxide to metal. Even when the Gooch crucible is protected from the burner flame by setting it in a circle of asbestos board in a larger porcelain crucible, one is not always able to extinguish the hydrogen flame readily. Experiments, made in an attempt to eliminate the use of carbon dioxide by cooling the sponge in hydrogen in order to simplify technic, showed that frequently the apparently cold metal would become warm and emit odors of tetroxide. The cause for such behavior was most probably the diffusion of air to the metal sponge through the holes in the bottom of the crucible.

For accurate work the Munroe crucible, which is of platinum and has a filter consisting of platinum sponge, was found to be preferable to the Gooch crucible with a filter of asbestos. A crucible of this kind was used in most of the experiments reported here. No precipitate was ever observed to have escaped this filter. A platinum cap, which fitted the bottom of the Munroe crucible, eliminated the necessity for a second protecting crucible. The ignition of the dioxide and the cooling of the resulting metal were greatly simplified when this type of crucible was used.

IX. RANGE OF pH VALUES OVER WHICH HYDRATED OSMIUM DIOXIDE IS COMPLETELY PRECIPITATED BY HYDROLYSIS

In a study on ruthenium it was found that for complete precipitation by hydrolysis the acidity of the solution could not deviate far from the value pH 6.0.

The qualitative experiments with osmium, described in a preceding section of this paper, indicated that a greater latitude of acidity was permissible for osmium and that complete precipitation occurred between pH 1.5 and 6.3. On either side of these limiting values the hydrated osmium dioxide tended to become colloidal. In order to confirm these qualitative observations, seven quantitative experiments were made in which known pH values were established by the use of indicator solutions. A solution of sodium bicarbonate was added to the boiling solutions containing the osmium until the indicator just changed color. The solutions were then boiled for about six minutes and filtered through a Munroe crucible. The precipitates were thoroughly washed with a hot 1 per cent solution of ammonium chloride, impregnated with saturated ammonium chloride, dried carefully, ignited in hydrogen, and the metal produced cooled to room temperature in carbon dioxide.

The complete transfer of the precipitate from the beaker to the crucible was effected by using a well-wetted policeman, since paper could not be used. Experience showed that this practice introduced no appreciable error into the determination. The filtrates from hydrolysis were found to be free from osmium when tested as previously described. The optimum pH for quick settling appeared to be about 4. This is the acidity at which brom phenol blue indicator changes from yellow to blue, and is the one which was always established in subsequent experiments.

The quantitative results are given in Table 2. The error in No. 21 was caused by a slight deflagration during ignition of the precipitate in hydrogen.

TABLE 2.—*Range of pH values over which hydrated osmium dioxide is completely precipitated by hydrolysis*

No.	$(NH_4)_2OsBr_6$ 28.06 per cent Os	$(NH_4)_2OsCl_6$ 39.28 per cent Os	Osmium present	Osmium recovered	Error	Indicator used	pH
	g	*g*	*g*	*g*	*g*		
18	0.4449		0.1248	0.1248	0.0000	Thymol blue	1.5
19	.4663		.1308	.1308	.0000	Brom phenol blue	4.0
20	.4599		.1290	.1289	−.0001	Brom cresol green	4.7
21	.4444		.1247	.1239	−.0008	Chlor phenol red	6.0
22	.4023		.1129	.1129	.0000	Brom cresol purple	6.3
23		0.2823	.1109	.1107	−.0002	Thymol blue	1.5
24		.2679	.1053	.1052	−.0001	Brom phenol blue	4.0

X. SEPARATION OF OSMIUM BY DISTILLATION AND RECOVERY BY HYDROLYSIS

The method developed in the foregoing experiments for the recovery of osmium is applicable to solutions which contain no other heavy metals. When other metals are present it becomes necessary first to make a separation of the osmium from these elements. The usual procedure described in the literature is to add nitric acid to such a solution, distil the osmium as tetroxide and absorb it in a solution of sodium hydroxide containing some alcohol.

Two experiments were made to test this method of separation by distillation with subsequent recovery of the osmium from the solution of sodium hydroxide. The apparatus used consisted of a

1-liter flask and four Erlenmeyer receiving flasks, each of 300 ml capacity. The entire apparatus was of glass and the various parts were connected by carefully ground joints. The distilling flask was provided with an inlet through which a slow current of air was passed during distillation and a thistle tube, having a stopcock, for the introduction of nitric acid. This stopcock was lubricated with vaseline. All other ground joints were sealed with a film of water. The evolved tetroxide was absorbed in a 10 per cent solution of sodium hydroxide to which one-fifth of its volume of alcohol was added. The absorption of the tetroxide appeared to be nearly complete in the solution in the first flask, and no osmium escaped the train of receiving solutions. The united solutions were digested on the steam bath for some hours to insure the complete reduction of the tetroxide. The osmium was recovered by hydrolysis in the manner previously described, after the alkaline solutions had been made acid with hydrochloric acid. In one experiment only about one-third of the osmium taken as ammonium bromoosmate was recovered. In the other experiment the recovered quantity was in excess of that taken by over 12 per cent. This abnormal result was found to have been caused by the presence of silica, dissolved from the glass by the hot alkaline solution. The osmium actually present in the contaminated precipitate, determined by difference on ignition in oxygen, was only 80 per cent of that originally taken. The incomplete recoveries were attributed to the presence of nitrates formed during the distillation of the osmium tetroxide. When the alkaline solutions were made acid with hydrochloric acid an indefinite amount of osmium must have escaped, since the filtrates from the hydrolytic precipitations showed no appreciable quantity of osmium.

While the removal of the osmium from the distilling flask was apparently complete and the absorption of the osmium tetroxide in the alkaline solutions quantitative, it did not appear hopeful to adapt the method of hydrolysis from acid solution to the final recovery of the osmium. It became necessary, therefore, to consider other absorbent solutions.

The use of hydrobromic acid in the preparation of bromoosmic acid suggested the possibility of using this reagent as an absorbent. Experiments, in which a 20 per cent solution of hydrobromic acid to which one-fifth of its volume of alcohol was added, proved definitely that absorption of osmium tetroxide in this reagent was not quantitative, even when the solutions were kept hot. The recoveries were found to be low by an amount varying from 5 to 24 per cent of the osmium taken, and appreciable quantities of osmium tetroxide were readily detected escaping the train of receiving solutions.

It was clearly apparent from the experiments with sodium hydroxide that the nitric acid which distilled with the tetroxide interfered in the subsequent recovery of the osmium. In order to eliminate this source of error it was necessary to destroy any nitric acid which entered the receiving solutions. In addition, it was advantageous to produce a solution to which the newly developed hydrolytic procedure could also be applied. A solution of both of these problems appeared to be offered by using 6 normal hydrochloric acid which had been saturated with sulphur dioxide.

Experiments were then made using this reagent as the absorbent. In the first experiment 0.1519 g of osmium as ammonium bromoosmate was taken. One hundred milliliters of water and 50 ml of nitric acid (specific gravity 1.42) were placed in the distilling flask. Each of three receiving flasks contained 75 ml of the absorbent reagent. The solution in the distilling flask was colorless after one hour. The complete absence of osmium in the residual nitric acid solution was proved, as previously outlined, by a negative test with thiourea when the nitric acid was destroyed by sulphur dioxide. No osmium was detected having escaped the train of receiving solutions. The contents of the three receiving flasks were united and evaporated on the steam bath to a volume of about 2 to 3 ml.[25] The quantity of osmium recovered by hydrolysis was 0.1497 g, or 98.55 per cent of the quantity taken.

In the second experiment 0.1735 g of osmium as ammonium bromoosmate was taken. Each of two receiving flasks contained 200 ml of the absorbent solution. The third flask, in this instance, was used for the detection of osmium by thiourea. Distillation was continued for 1 hour, 10 minutes. No osmium escaped the second receiving flask, but a small quantity, estimated by the intensity of color developed with thiourea to be about 0.00024 g, was found in the nitric-acid solution after distillation was thought to be complete. There was recovered from the solution in the first receiving flask 0.1677 g of osmium, and from that in the second receiving flask 0.0030 g of osmium. The remaining 0.0026 g of osmium could not be accounted for.

In the third experiment 0.1106 g of osmium as ammonium bromoosmate and, in addition 0.1 g of iridium as ammonium chloroiridate, were taken. In this and in subsequent experiments the quantity of nitric acid used was reduced to 20 ml. At the end of one hour the solutions in the three receiving flasks were replaced by fresh solutions of 6 normal hydrochloric acid saturated with sulphur dioxide. Distillation was then continued for three-fourths hour. No color developed in the second set of solutions and, on evaporation of these solutions to a volume of about 5 ml, thiourea detected no osmium present. From the first set of absorbing solutions 0.1094 g of osmium was recovered, less than the quantity taken by 0.0012 g.

In a fourth experiment 0.0956 g of osmium as ammonium chloroosmate, together with a total quantity, 0.3 g, of Pt, Ir, Rh, and Pd as chlorides, was taken. The distillation was continued for seven hours, using four renewals of absorbent solution. The unexpectedly slow distillation of osmium from the chloroosmate will be discussed in a later section. The quantity of osmium recovered from the united receiving solutions was 0.0929 g, differing from the quantity taken by 0.0027 g.

In these experiments an error, amounting usually to less than about 2.5 mg of osmium, irrespective of the quantities of osmium taken, continued to occur in the recovery of osmium by distillation with nitric acid.

[25] It may occur to the reader that the osmium could be recovered from the absorbent solution more simply by igniting the evaporated residue under hydrogen without resorting to a hydrolytic precipitation. In such a procedure it would be necessary to neutralize the sulphuric acid present. This could be done by adding a slight excess of ammonium chloride during evaporation. The subsequent evaporation and drying of the salt mixture in a crucible, simple as it at first appears, is very troublesome, however, because of the marked tendency of the ammonium salts to creep. Furthermore, this creeping would enhance the danger of loss of osmium. Also such a method of treatment would not eliminate impurities in the form of soluble salts introduced through the reagents used and would be wholly unsuitable if applied as a general method to solutions containing appreciable quantities of alkali salts. The recovery of osmium by hydrolysis, on the other hand, obviates these difficulties without requiring additional time.

XI. EXPERIMENTS TO LOCATE THE SOURCE OF ERROR IN THE DETERMINATION OF OSMIUM BY DISTILLATION FROM SOLUTION WITH NITRIC ACID

While the results obtained when 6 normal hydrochloric acid saturated with sulphur dioxide was used as an absorbent solution were gratifying, they were not quantitatively satisfactory. There repeatedly appeared a small but significant error, the cause of which was not immediately apparent. Precaution had been taken to flush frequently the tube used for the introduction of nitric acid into the distilling flask so that it was not likely that the discrepancies in recovery were occasioned by loss of tetroxide diffusing into this tube. A new distilling and receiving apparatus, meanwhile, was so constructed that the possibility of loss of osmium tetroxide by leakage was thought to have been eliminated. Experiments were repeated with this new apparatus and again errors of the same magnitude as those previously observed were obtained.

Attention was then turned to another possible cause for the error observed; namely, loss of osmium as tetroxide when the absorbent solutions were evaporated on the steam bath. If this were the cause, losses of osmium should occur with solutions made to approximate in composition those actually obtained on distillation.

Two series of such solutions were prepared. In the one, portions of ammonium chloroosmate and of ammonium bromoosmate were each dissolved in 250 ml of 6 normal hydrochloric acid and the solutions evaporated on the steam bath until dry residues of salt were obtained. These residues were dissolved in 150 ml portions of water, the solutions heated to boiling, and the osmium precipitated by hydrolysis at pH 4.0. The precipitates were filtered on a Munroe crucible, washed with a hot 1 per cent solution of ammonium chloride, impregnated with saturated ammonium chloride, ignited in hydrogen, cooled in carbon dioxide and weighed. The results, given in Table 3, showed that no significant losses of osmium occurred under these conditions.

TABLE 3.—*Recovery of osmium from solutions of ammonium chloroosmate and of ammonium bromoosmate in 6 normal HCl evaporated to dryness*

No.	$(NH_4)_2OsBr_6$	$(NH_4)_2OsCl_6$	Osmium present	Osmium present	Osmium recovered	Error
	g	*g*	*Per cent*	*g*	*g*	*g*
25	----------	0.2584	43.41	0.1121	0.1124	+0.0003
26	0.3537	----------	28.06	.0993	.0993	.0000
27	.5041	----------	26.94	.1358	.1357	−.0001
28	.6407	----------	26.94	.1726	.1725	−.0001

In the second series, solutions were made so as to duplicate those obtained when the distilled osmium tetroxide was absorbed in 6 normal hydrochloric acid saturated with sulphur dioxide. For this purpose, portions of ammonium bromoosmate were added to solutions composed of 250 ml of 6 normal hydrochloric acid, 2 ml of sulphuric acid (specific gravity 1.84) and 100 ml of water which had been saturated with sulphur dioxide. These solutions were allowed to remain on the steam bath for several hours after no further evaporation occurred. The solutions, which were sirupy because of the sulphuric

acid present, were diluted to 150 ml with water and the osmium recovered as above described. The sirupy solutions, previous to dilution, were frequently smelled, but no odor of tetroxide was ever observed. The recoveries of osmium obtained, shown in Table 4, were practically quantitative in 2 of the 6 experiments, but in the other 4 were low by amounts which approximated those previously observed.

TABLE 4.—*Recovery of osmium from solutions of ammonium bromoosmate in 6 normal HCl to which H_2SO_4 and SO_2 were added*

No.	$(NH_4)_2OsBr_6$ 26.91 per cent Os	Osmium present	Osmium recovered	Error
	g	*g*	*g*	*g*
29	0.4624	0.1244	0.1245	+0.0001
30	.4974	.1339	.1325	−.0014
31	.5032	.1354	.1334	−.0020
32	.4691	.1262	.1248	−.0014
33	.4574	.1231	.1213	−.0018
34	.4640	.1249	.1246	−.0003

It seemed strange, if losses of osmium occurred on evaporation, especially when the solutions became sirupy, that they showed no particular increase when the concentrated solutions were allowed to remain on the steam bath. If the sulphuric acid present were really responsible for the discrepancy between the quantity of osmium taken and that recovered, it was thought that neutralization of the acid by the formation of sulphate might decrease the magnitude of the error. Consequently, portions of ammonium bromoosmate were dissolved in solutions composed of 250 ml of 6 normal hydrochloric acid, 2 ml of sulphuric acid (specific gravity 1.84), and 100 ml of water which had been saturated with sulphur dioxide. In order to provide for the neutralization of the sulphuric acid when the solutions became concentrated, 5 g of sodium chloride was added to each of four solutions and 5 g of ammonium chloride to each of two solutions. These salts were added in the form of filtered solutions. The six solutions were allowed to evaporate to dryness and the beakers were then left several hours on the steam bath. The dried residues were dissolved in water as before and the osmium recovered by hydrolysis in the manner already described. The recoveries, as shown in Table 5, were nearly complete in three of the experiments, but in the other three were low by amounts approximating those previously observed.

TABLE 5.—*Recovery of osmium from solutions of ammonium bromoosmate in 6 normal HCl to which H_2SO_4, SO_2, NaCl and NH_4Cl were added*

No.	$(NH_4)_2OsBr_6$	Osmium present	Osmium present	Osmium recovered	Error	
	g	*Per cent*	*g*	*g*	*g*	
35	0.3716	26.91	0.1000	0.0974	−0.0026	
36	.4697	26.91	.1264	.1264	.0000	NaCl.
37	.3847	26.94	.1036	.1034	−.0002	
38	.4288	26.94	.1155	.1152	−.0003	
39	.5044	26.94	.1359	.1329	−.0030	NH_4Cl.
40	.5266	26.94	.1419	.1408	−.0011	

The sole remaining source of error was the incomplete precipitation of the osmium on hydrolysis. It had been previously established by experiment that no significant amount of osmium remained in the filtrates, but the conditions were different in that no sulphur dioxide had ever been present. The filtrates obtained in the experiments reported in Tables 3, 4, and 5 were now carefully searched for the presence of osmium. These filtrates were water clear and showed no evidence of osmium dioxide depositing on standing. Each filtrate in turn was completely transferred to the distilling apparatus. Twenty milliliters of nitric acid (specific gravity 1.42) was added and the solution heated to boiling for one-half hour while a slow current of air was passed. The distillate, in each instance, was led into 50 ml of 6 normal hydrochloric acid saturated with sulphur dioxide to which thiourea was added. When the solutions were heated on the steam bath intensities of color developed which corresponded to the magnitude of the observed errors. The results obtained are assembled in Table 6.

TABLE 6.—*Detection of osmium in the filtrates from hydrolysis of absorbent solutions containing sulphur dioxide*

No.	Error	Color produced by reaction with thiourea
	g	
25	+0.0003	Colorless.
26	.0000	Do.
27	−.0001	Faint pink.
28	−.0001	Colorless.
29	+.0001	Faint pink.
30	−.0014	Red.
31	−.0020	Strong red.
32	−.0014	Red.
33	−.0018	Do.
34	−.0003	Faint pink.
35	−.0026	Strong red.
36	.0000	Colorless.
37	−.0002	Faint pink.
38	−.0003	Do.
39	−.0030	Deep red.
40	−.0011	Red.

XII. COMPLETE RECOVERY OF OSMIUM FROM SOLUTIONS OF HYDROCHLORIC ACID WHICH HAVE CONTAINED SULPHUR DIOXIDE

The source of the slight error in the determination of osmium, when the solution consisting of 6 normal hydrochloric acid saturated with sulphur dioxide was used for the absorption of the evolved tetroxide, was thus traced to the incomplete precipitation of the osmium on subsequent hydrolysis. The cause of the incomplete precipitation was attributed to the presence of a small quantity of an undecomposed sulphite compound of osmium. It had been demonstrated that if no sulphur dioxide was used, precipitation was quantitative and that no significant amount of osmium remained in the filtrate. Furthermore, in considering various reagent solutions to absorb osmium tetroxide, it was observed that while a solution of sodium sulphite completely absorbed the tetroxide only a very slight precipitate was obtained on subsequent hydrolysis.

In order, then, to effect quantitative precipitation it would be necessary to insure the complete destruction of any sulphite compounds of osmium. Accordingly, three solutions were prepared, containing ammonium bromoosmate, hydrochloric acid, sulphuric acid, sulphur dioxide, and water as previously described, and evaporated as far as possible on the steam bath. Each sirupy residue was digested for about 15 minutes with 10 ml of hydrochloric acid (specific gravity 1.18) and again evaporated. The digestion with 10 ml of hydrochloric acid and evaporation were repeated. The residues from the last evaporation were diluted with 150 ml of water. During precipitation the solutions were purposely maintained at nearly boiling temperature for approximately four hours while the bicarbonate was being added. This was done, incidentally, to confirm previous observations that no loss of osmium as osmium tetroxide occurred during hydrolysis. When the brom phenol blue indicator present turned faintly blue, the solutions were boiled six minutes.

The precipitate in experiment No. 41 was filtered immediately. Those in Nos. 42 and 43 were not filtered until 48 hours later. Just previous to filtration these latter two were again boiled for five minutes. The metallic residues from Nos. 42 and 43 were well washed with a hot 1 per cent solution of ammonium chloride and ignited again in hydrogen. The weights remained constant, showing that the washing of the original precipitate had been complete. The three filtrates were tested for osmium as previously described. A faint pink color developed in each instance which corresponded to a quantity of osmium far less than 0.0001 g.

The results, given in Table 7, which were later confirmed by experiments described in Section XIV, showed that digestion of the sirupy residue with hydrochloric acid eliminated the cause of error. Incidentally, the results given in Table 7 showed that no osmium was lost on prolonged boiling of the solutions during the neutralization of excess acid by sodium bicarbonate.

TABLE 7.—*Complete recovery of osmium from solutions of HCl which have contained* SO_2

No.	$(NH_4)_2OsBr_6$ 26.94 percent Os	Osmium present	Osmium recovered	Error
	g	*g*	*g*	*g*
41	0.6712	0.1808	0.1806	−0.0002
42	.5136	.1384	.1385	+.0001
43	.5025	.1354	.1354	.0000

XIII. PRECIPITATION OF OSMIUM IN THE PRESENCE OF SODIUM SALTS

The hydrolytic precipitation of osmium as the hydrated dioxide necessarily always occurred in the presence of varying amounts of sodium chloride or of sodium sulphate, produced by neutralization with sodium bicarbonate of the corresponding acid present in the solutions. These precipitates were always washed thoroughly with a hot 1 per cent solution of ammonium chloride. In nearly every instance the metallic residues obtained after ignition in hydrogen were also washed with this reagent solution and reignited. No

significant differences were ever found in the weights obtained. It thus appeared that a single thorough washing removed all sodium salts. Furthermore, the washing never caused the precipitate to become colloidal.

XIV. SEPARATION OF OSMIUM FROM THE OTHER PLATINUM METALS BY DISTILLATION FROM NITRIC-ACID SOLUTION

With a reliable method at hand for the recovery of osmium from a suitable absorbing solution, the investigation was now extended to the matter of the quantitative separation of osmium from the other platinum metals by distillation as osmium tetroxide. Methods for the determination of osmium, involving the separation of osmium from accompanying metals by distillation as tetroxide from nitric-acid solution, are frequently mentioned in the literature and it has been usually assumed that the separation is complete. However, no specific data resulting from critical experiments could be found to verify this assumption.

To make certain, first of all, that no significant quantities of the platinum metals reached the receiving flasks, either by distillation or by entrainment, a solution containing 0.100 g of platinum, 0.106 g of iridium, 0.082 g of rhodium, and 0.020 g of palladium, as chlorides, was placed in the distilling flask with 150 ml of water and 20 ml of nitric acid (specific gravity 1.42) and boiled for one hour while a slow current of air was passed. The absorbing solution, consisting of 6 normal hydrochloric acid, was evaporated nearly to dryness and diluted with 5 ml of water. No evidence of precipitation was obtained when this colorless solution was treated with hydrogen sulphide. A second solution, containing approximately 0.1 g of ruthenium as chloride, was treated similarly, boiling being continued for two hours, and the distilled vapors caught in 6 normal hydrochloric acid containing some alcohol. The receiving solution was evaporated twice with concentrated hydrochloric acid and finally diluted with 10 ml of water. The thiosulphate test, which is sensitive to extremely small quantities of ruthenium, was applied but no color developed.

Two experiments were made in which osmium was separated from the other five platinum metals by distillation from nitric-acid solution. The quantities of these other metals taken for each experiment were 0.100 g Pt, 0.200 g Ir, 0.016 g Rh, 0.020 g Pd, and 0.075 g Ru. The osmium was distilled from a solution whose volume was 170 ml, of which 20 ml was nitric acid (specific gravity 1.42). The evolved tetroxide was absorbed in 6 normal hydrochloric acid saturated with sulphur dioxide and the metal recovered as previously described. The residual solutions from the distillation yielded no trace of osmium upon further distillation and were in all probability completely free from osmium. In the first experiment, of 0.1608 g of osmium, taken as ammonium bromoosmate, 0.1606 g was recovered. The filtrate obtained upon the precipitation of the hydrated dioxide showed the presence of a minute quantity of osmium, but very much less than 0.0001 g. In the second of these two experiments the quantity of osmium recovered was only 0.2047 g while that taken was 0.2076 g. From 0.002 to 0.0025 g of osmium was found in the filtrate from hydrolysis. The appearance of this quantity of osmium in the filtrate

indicated that the complete destruction of sulphite compounds had probably not been effected previous to hydrolysis. Consequently, two more determinations were made and particular attention was paid to the evaporation of the absorbent solutions. Four additions of concentrated hydrochloric acid were made, instead of two, and each time digestion was prolonged for 15 minutes while the beakers were covered before allowing the solutions to evaporate. The quantities of osmium taken as ammonium bromoosmate were 0.1390 and 0.1548 g and those recovered were 0.1388 and 0.1546 g. No osmium appeared to remain in the residual platinum metal solutions. One of the filtrates yielded a very faint pink color when tested for osmium by distilling into a thiourea solution while the other gave no indication of the presence of osmium.

These results show that the separation of osmium from the other platinum metals by distillation as tetroxide from nitric-acid solution is complete, and that if care is taken to insure total decomposition of sulphite compounds formed during absorption of the tetroxide the recoveries are also quantitative within experimental error.

XV. INCIDENTAL EXPERIMENTS

The elimination of osmium from solutions of ammonium bromoosmate by dilute nitric acid was usually found to be complete within one hour, while the elimination of osmium from solutions of ammonium chloroosmate, under similar conditions, was complete only after seven or eight hours. In an attempt to shorten the time required to effect the separation of osmium from the chloroosmate a number of experiments were made in which the nature or composition of the solution was altered. In addition, observations were also made regarding the behavior of the other platinum metals.

1. DISTILLATION FROM A MIXTURE OF SULPHURIC AND NITRIC ACIDS

A solution containing approximately 0.075 g of osmium as ammonium chloroosmate, 10 ml of sulphuric acid (specific gravity 1.84), 6 ml of 6 normal nitric acid and 25 ml of water was heated in an open beaker. The solution, which emitted heavy vapors of sulphuric acid after 10 minutes, was diluted to 20 ml with water and tested for osmium with thiourea. The complete absence of osmium was demonstrated. The experiment was repeated with a distilling apparatus. At the end of 1 hour the residual solution was colorless and gave no test for osmium with thiourea. The experiment was then repeated in an open beaker, using ammonium bromoosmate instead of ammonium chloroosmate. Again, the osmium was found to be easily eliminated and no osmium remained in the sulphuric acid solution.

When a solution of ruthenium was treated as just described, it was found that as the sulphuric acid approached the fuming stage ruthenium slowly distilled, and that if heating were continued a black deposit appeared in the distilling flask and delivery tube. The successive additions of nitric acid dissolved the black deposit previously formed and caused more and more ruthenium to reach the absorbent solution.

Iridium, taken as ammonium chloroiridate, when treated in the same manner as that described for ruthenium, remained entirely in the distilling flask as a soluble green compound.

2. DISTILLATION FROM SULPHURIC ACID

The experiments which have just been described were repeated with the exception that no nitric acid was used. Here it was found that osmium, originally present as ammonium chloroosmate, was readily and completely eliminated when the solution was heated to the fuming point of sulphuric acid, while that present as ammonium bromoosmate was only partially distilled, the mass remaining in the flask, and likewise in the beaker, as a black deposit. Continued heating for several hours failed to distill more than a small proportion of the osmium taken as bromoosmate.

It was further found that no trace of ruthenium distilled when sulphuric acid alone was used, nor did any iridium. Both of these metals remained in the distilling flask as soluble compounds.

3. DISTILLATION FROM NITRIC ACID

In these experiments the osmium was distilled from concentrated nitric acid. From ammonium bromoosmate the osmium was completely distilled in about 10 minutes while from ammonium chloroosmate the osmium was entirely eliminated only after one and three-fourths hours.

When ruthenium as ammonium nitrosopentachlororuthenate was heated with 100 ml of concentrated nitric acid until 20 ml was volatilized, it was repeatedly found that an appreciable amount distilled. A purplish color was observed in the condensing vapors which passed over at first. Further heating, however, did not cause this phenomenon to continue, nor was ruthenium eliminated at all rapidly from the distilling flask. Noyes and Bray [26] report the observation that no ruthenium distills when a solution containing 4 ml of concentrated nitric acid, 3 ml of residual bromide solution, and 3 ml of water is heated in a distilling flask until 4 ml of liquid has been removed, but that if 2 ml more of liquid is distilled, from 0.0001 to 0.0002 g of ruthenium passes into the distillate. Two experiments were made in which the above conditions were established, but ten times the quantities of materials were used. The vapors were absorbed in 6 normal hydrochloric acid which was constantly saturated with a current of sulphur dioxide. No ruthenium was detected in the first 40 ml of distillate, either by thiourea or by sodium thiosulphate, even when the solutions were concentrated by evaporation to volumes of 5 to 10 ml. A small quantity of ruthenium was found in the next 20 ml of distillate by thiourea in one of the experiments, but the amount was much less than 0.0001 g. No ruthenium could be detected in the second 20 ml portion in the other experiment. A third experiment was made in which no hydrobromic acid was added to the distilling flask. No ruthenium was detected in either portion of distillate by thiourea or by sodium thiosulphate. The distillations were run so that the first 40 ml required about 1 hour 20 minutes and the next 20 ml about 40 minutes.

4. DISTILLATION FROM ALKALINE SOLUTION ACIDIFIED WITH NITRIC ACID

When a metallic material such as osmiridium is fused with a molten mixture of alkali hydroxide and nitrate, the osmium present

[26] Noyes and Bray, Qualitative Analysis for the Rare Elements, The Macmillan Co., p. 41; 1927.

is converted to a soluble osmate. Since this is the form in which the osmium is obtained in the analysis of crude platiniferous material, the following experiment was made to determine the behavior of the osmium on acidification of the solution with nitric acid. It has been generally assumed that the elimination of the osmium as osmium tetroxide under these conditions is quantitative.

Approximately 0.1 g of osmium sponge was added to a molten mixture of 10 g of sodium hydroxide and 1 g of sodium nitrate contained in a gold crucible. The cold alkaline mass was dissolved in 75 ml of water and transferred to the distilling apparatus. A total of 36 ml of nitric acid (specific gravity 1.42) was added and the final volume of the solution became 170 ml. The excess nitric acid produced a colorless solution from which the osmium was easily distilled. The complete absence of osmium in the residual 150 ml of solution was demonstrated, first, by carefully decomposing the nitric acid in a 50 ml portion with sulphur dioxide and testing with thiourea, and, second, by heating a 50 ml portion in a distilling flask and absorbing the vapors in hydrochloric acid, containing thiourea, saturated with sulphur dioxide.

The above experiment was repeated, this time with the addition of 0.093 g of pure iridium sponge. The metallic iridium was added to a molten mixture of 10 g of sodium hydroxide and 2 g of sodium nitrate and appeared to be quite rapidly attacked when the alkaline bath was at a red heat. The melt was maintained at this temperature for 30 minutes, allowed to cool and dissolved, as before, in 75 ml of water. The osmium present was separated in the same manner as described above. At the end of 45 minutes the contents of the distilling flask, consisting of a pale green solution and a black deposit, were transferred to a second distilling flask and heated for 25 minutes. The vapors which distilled were absorbed in a solution of 6 normal hydrochloric acid and thiourea which was saturated with sulphur dioxide. No color developed in this thiourea solution.

To determine whether any osmium was retained by the insoluble iridium compound, the black residue was separated from the supernatant liquor by careful decantation. Twenty millimeters of concentrated sulphuric acid and 2 ml of concentrated nitric acid were added to the flask and the mixture heated for 30 minutes until heavy fumes of sulphuric acid appeared. The distilled vapors, absorbed in a solution containing thiourea, again produced no color. Finally, the insoluble iridium compound was carefully separated from the sulphuric-acid solution by decantation, transferred to a gold crucible, dried by evaporation on the steam bath, and subjected to a second fusion. Upon acidification with nitric acid and distillation, a quantity of osmium, estimated to be not more than 0.0001 g by comparison with solutions of known osmium content, was detected in the thiourea solution.

The foregoing experiments disclosed some rather surprising facts regarding the behavior of chloroosmate and of bromoosmate toward nitric acid and toward sulphuric acid. It was found that chloroosmate was quite stable toward nitric acid, even when the acid was hot and concentrated, but was readily decomposed with complete elimination of osmium by hot concentrated sulphuric acid. On the other hand, bromoosmate was quickly decomposed and the osmium eliminated by nitric acid, both dilute and concentrated, but scarcely

affected by hot concentrated sulphuric acid. A mixture of the two acids, however, quickly eliminated the osmium from either compound. It was further found that while ruthenium did not separate as a volatile compound from hot concentrated sulphuric acid alone, it did so if some nitric acid was present. In addition, it was observed that a small but appreciable quantity of ruthenium distilled from concentrated nitric acid, but that no ruthenium was eliminated from solutions containing nitric acid up to 40 per cent by volume. Under the conditions above mentioned, iridium, which may be taken as representing the remaining members of the platinum group, did not appear in the distillate, but remained as a soluble compound in the distilling flask.

From solutions of sodium osmate, the form in which osmium is obtained during solution of metallic material in fused alkaline reagents, it was found that the osmium was easily and completely eliminated on acidifying with nitric acid.

It may thus be seen that the method of separation chosen will depend upon the composition of the solution from which the osmium is to be distilled and also upon the presence or absence of ruthenium.

XVI. SUMMARY OF RESULTS OBTAINED

1. Osmium, when present as a chloride or bromide, can be quantitatively precipitated as a hydrated dioxide from boiling solutions having a pH range from 1.5 to 6.3.

2. The presence of alkali chloride or sulphate during precipitation of the hydrated dioxide introduces no error into the determination. The alkali salts can be completely removed from the precipitate by washing.

3. There is a marked tendency to deflagrate when the hydrated dioxide is heated, even in the presence of hydrogen, with accompanying mechanical loss of osmium. This tendency is entirely overcome if the precipitate is impregnated with ammonium chloride.

4. The best filtering device for hydrated osmium dioxide is the Munroe crucible, but carefully prepared asbestos filters can be used for accurate determinations.

5. Osmium, which has been reduced in hydrogen and cooled to room temperature in carbon dioxide, remains unattacked by the air for a surprisingly long time. No error is introduced when it is inconvenient to make weighings immediately.

6. Osmium, when originally present as bromoosmate or as alkaline osmate, can be easily and completely eliminated as osmium tetroxide from boiling solutions containing approximately 10 per cent of nitric acid by volume. That present as chloroosmate, while it can be eliminated completely if distillation be continued for a long time, is not readily removed even by boiling concentrated nitric acid. Osmium, present as chloroosmate, is quickly separated as the tetroxide, however, from concentrated sulphuric acid near the boiling point of the acid, while that present as bromoosmate remains for the most part in the sulphuric-acid solution. When a mixture of sulphuric and nitric acids is used, osmium is readily eliminated from either type of compound.

7. No ruthenium is eliminated from boiling solutions containing nitric acid up to 40 per cent by volume nor from concentrated sul-

phuric acid alone, but, it is separated gradually from concentrated sulphuric acid containing nitric acid. A small but appreciable quantity of ruthenium is eliminated by boiling concentrated nitric acid.

8. The four remaining members of the platinum group do not appear in the distillate under the conditions described.

9. A solution of 6 normal hydrochloric acid saturated with sulphur dioxide is a very suitable reagent for the quantitative recovery of distilled osmium tetroxide.

10. A slight error is introduced unless the evaporated absorbent solution is digested and evaporated with concentrated hydrochloric acid a sufficient number of times to insure complete decomposition of sulphite compounds of osmium.

11. The thiourea test for the detection of osmium, described by Chugaev and said by him to be sensitive to 1 part in 100,000, can be

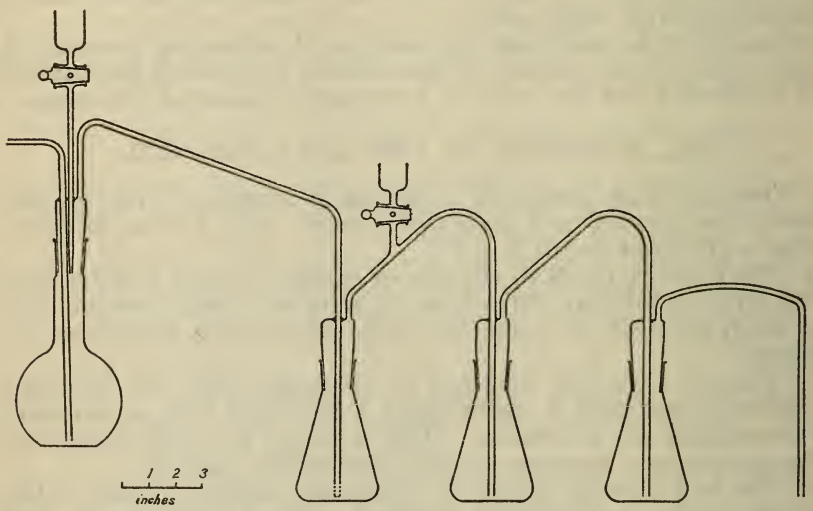

FIGURE 2.—*Distilling flask with train*

made much more sensitive: 0.02 mg of osmium in 100 ml (1 part in 5,000,000 parts of solution) can be detected. The test can be applied to solutions containing nitric acid if an excess of sulphur dioxide is first added.

XVII. METHOD OF ANALYSIS RECOMMENDED

The following procedure is designed to separate osmium as the volatile tetroxide from a solution containing the platinum group of metals; to recover the evolved tetroxide by absorption in 6 normal hydrochloric acid which has been saturated with sulphur dioxide; to precipitate the osmium as hydrated dioxide from the absorbent solution; and to obtain the osmium as metal.

1. DISTILLING APPARATUS

The distilling apparatus is shown in Figure 2. It consists of three main parts, namely, a 700 ml distilling flask, a set of three 300 ml

absorbing flasks, and a train of inlet and delivery tubes which are sealed into one rigid piece. The thistle tube closed by a stopcock, placed between the first and second absorbing flasks, serves to replenish the absorbing solution if an unusual amount of nitric acid is distilled and also, at the end of the distillation, to rinse the tube connecting the two flasks. The entire apparatus is constructed of pyrex glass. The joints must be very carefully ground, and are preferably uniform so that the flasks are interchangeable. It is important to note that these joints are sealed with a film of water only and not with lubricating grease, because the latter causes reduction of some osmium tetroxide to dioxide, which can not be readily recovered. It was found necessary to grease the stopcock in the tube used for the introduction of nitric acid into the distilling flask, but this constitutes the only exception. During operation, this delivery tube is frequently flushed with water to remove any osmium tetroxide which may have diffused into it. The diameter of this tube should be such that a column of water will be held. Three absorbing flasks are used but the absorption of osmium tetroxide is practically complete in the first flask and no osmium escapes the second flask.

2. PROCEDURE

Place 150 ml of 6 normal hydrochloric acid, which has been freshly saturated with sulphur dioxide, in the first absorbing flask and 50 ml of the same reagent solution in each of the other two flasks. Place the solution containing the osmium in the distilling flask and make sure that the separate parts of the entire apparatus are properly connected. If necessary, dilute the solution in the distilling flask to about 100 ml with water and add through the inlet tube 40 ml of nitric acid (1 volume of acid, specific gravity 1.42, diluted with 1 volume of water). Flush the thistle tube and stopcock with 10 ml of water. Pass a slow current of air through the apparatus and heat the solution in the distilling flask to boiling. Continue the distillation for one hour. This length of time should be sufficient to insure complete elimination of osmium from solutions in which the osmium is originally present as alkaline osmate or as bromoosmate. If, however, the osmium is present as chloroosmate the time required will be from seven to eight hours. In this case it is preferable to distil from concentrated sulphuric acid, or, if ruthenium is known to be absent, from concentrated sulphuric acid to which a few milliliters of nitric acid is added. Unite the portions of the absorbent solution and evaporate as far as possible on the steam bath in a clean unetched beaker. Digest the residue with 10 ml of hydrochloric acid (specific gravity 1.18) for 15 minutes and evaporate a second time. Repeat the digestion with hydrochloric acid and the evaporation three times more. This is done to insure complete decomposition of any sulphite compounds of osmium. Take up the residue from the last evaporation with 150 ml of water and heat to boiling. Add a solution of sodium bicarbonate, free from insoluble matter, until a precipitate appears and suddenly coagulates. Add a few drops of brom phenol blue indicator. Then add sufficient bicarbonate solution to produce a faint bluish color and boil five to six minutes.

Filter through a Munroe crucible, carefully pouring the supernatant liquid through first. Transfer the precipitate and wipe the

inner walls of the beaker and also the glass rod with a rubber policeman which has been well wetted. Wash thoroughly with a hot 1 per cent solution of ammonium chloride. Cover the precipitate with solid ammonium chloride. Moisten the ammonium chloride with a few drops of the wash solution and saturate the precipitate by suction. If desired, a saturated solution of ammonium chloride may be used to impregnate the precipitate. Continue the suction until the bottom of the crucible is coated with solidified ammonium chloride.

Wipe off this coating of salt and place the platinum cap on the bottom of the crucible. Cover the crucible with a Rose lid, preferably of quartz. Ignite a stream of hydrogen from a Rose delivery tube, likewise of quartz, and regulate the stream so that a very small flame is produced. Then insert the Rose tube through the opening in the Rose lid. The hydrogen flame will probably become extinguished by this operation and must be reignited. This is done by momentarily placing a burner flame under the crucible. The hydrogen will now burn as it issues from under the lid at the edge of the crucible. After five minutes gradually heat the crucible until all ammonium chloride is expelled. Ignite the osmium residue strongly in hydrogen for 10 minutes. Remove the burner and allow the crucible to cool somewhat. Extinguish the hydrogen flame by momentarily breaking the current of hydrogen and allow the crucible to cool to room temperature. Finally displace the hydrogen with a current of carbon dioxide and weigh as metallic osmium.

XVIII. ACKNOWLEDGMENTS

Asknowledgment is made to Edward Wichers for many helpful suggestions. The writer wishes also to express his appreciation to E. W. Zimmerman for the sketches of the apparatus shown.

Washington, January 21, 1931.

7/13/54

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